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14. ABSTRACT

During this project we have optimized the performance of alpha-SiAlON with respect to the following properties; hardness, fracture toughness, room temperature strength, high temperature strength, oxidation resistance, and machinability. Strong correlations between some of these properties have been found. For example, a positive correlation between fracture toughness and room temperature strength, a positive correlation between high temperature strength and oxidation resistance, a negative correlation between hardness and machinability, and a negative correlation between fracture toughness and high temperature strength. By controlling composition and microstructure, optimization of a subset of properties have been achieved. Various alpha-SiAlONs thus optimized are suitable for applications that call for different, tailorable properties.

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DESIGNED CERAMICS FOR AEROSPACE APPLICATIONS

AFOSR GRANT NUMBER F49620-01-1-0150

Final report, January 2005

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Research Objectives

Basic research on the physical chemistry, processing, and mechanical properties of nitride and oxide ceramics with designed microstructures for toughening is conducted. The emphasis is on high temperature ceramics, especially those of light elements. Ceramics investigated include α-SiAlON and o-SiAlON with acicular grains, alumina/zirconia laminar/cellular composites, and Si_3N_4/SiC composites with interpenetrating phases.

Accomplishments

Development of α-SiAlON

We have optimized the performance of α-SiAlON with respect to the following properties, hardness, fracture toughness, room temperature strength, high temperature strength, oxidation resistance, and machinability. Strong correlations between some of these properties have been found. For example, a positive correlation between fracture toughness and room temperature strength, a positive correlation between high temperature strength and oxidation resistance, a negative correlation between hardness and machinability, and a negative correlation between fracture toughness and high temperature strength. By controlling composition and microstructure, optimization of a subset of properties have been achieved. Various α-SiAlONs thus optimized are suitable for applications that call for different properties. These results are summarized below, emphasizing the use of additives.

<u>Optimization of Fracture Toughness, Room Temperature Strength and Hardness</u>

Our pioneering work has illustrated the dramatic improvement in fracture toughness of α-SiAlON due to the formation of elongated grains. This was achieved by seeding and by the selection of stabilizing cations. We have now established that F is an essential additive that facilitates grain boundary decohesion during crack propagation resulting in high fracture toughness. F addition has a relatively small effect on hardness, but it greatly enhances densification. As a result, high fracture toughness, high room temperature strength and high hardness can be simultaneously obtained. Further optimization has been achieved by the addition of oversized cations, such as La, Sr, Ba, and K that do not enter the network structure of α-SiAlON. These ceramics consistently have a room temperature strength of 800-1000 MPa, a toughness of 8-12 $MPam^{1/2}$, and a hardness of 19-21 GPa. They are suitable for structural applications below 1000°C.

<u>Optimization of High Temperature Strength, Room Temperature Strength and Hardness</u>

We have found undoped α-SiAlON to be excellent in oxidation and high temperature creep resistance. This establishes, for the first time, the concept that Al incorporation is not detrimental to the grain boundary properties of α-SiAlON, unlike the case of β-Si_3N_4. However, undoped α-SiAlON has low room temperature strength because of poor densification. We have found, for the first time, that La_2O_3 is an effective additive to substantially improve densification of α-SiAlON with relatively little effect on high temperature strength. The fracture toughness of these ceramics, however, is not sensitive to microstructure, which can be readily modified by seeding. This is because of the high decohesion strength of the grain boundary. These ceramics consistently have a room temperature strength of about 800 MPa, a high temperature strength (at 1300°C) of 600 MPa, a toughness of 5-7 $MPam^{1/2}$, and a hardness of 21-22 GPa. They are suitable for structural applications at below 1300°C in inert or moderately oxidizing environment.

Optimization of Oxidation Resistance, High Temperature Strength and Hardness

We have found that at 1300°C in air and in Na-containing environments, α-SiAlON has excellent oxidation resistance, better or at least comparable to that of the SN282 (from Kyocera), which is the state-of-the-art turbine-grade β silicon nitride. Such oxidation resistance is severely compromised by F addition, though. The La addition, which facilitates densification, has a less, but still adverse, effect on oxidation resistance. However, we have now discovered that, in both F- and La-containing α-SiAlONs the oxidation resistance can be restored by the addition of AlN: at 10% AlN addition, the oxidation resistance (in terms of oxide layer thickness after air exposure for 24 hours) at 1300°C is improved by one order of magnitude. On the other hand, the addition of AlN retards densification, thus lowering the room temperature strength. It also suppresses the growth of elongated grains, resulting in a low fracture toughness. These ceramics have a typical room temperature strength of about 500 MPa, a high temperature strength (at 1300°C) of 400 MPa, a toughness of 5 $MPam^{1/2}$, and a hardness of 21-22 GPa. They are suitable for structural applications at 1300°C in oxidizing environment.

Optimization of Machinability, Room Temperature Strength and High Temperature Strength

Using nanocrystalline BN additive, we have obtained machinable α-SiAlON for the first time. The BN addition also has a dramatic effect of lowering hardness, but it maintains the strength at room temperature and high temperature. This is because of the rather uniform microstructure achieved by the very fine BN dispersion and the apparently favorable grain boundary chemistry. A typical machinable α-SiAlON containing 20% BN has a room temperature strength of 800 MPa, and a fracture toughness of 4.5 $MPam^{1/2}$. Such ceramics are suitable for structural applications up to 1000°C in inert and moderately oxidizing atmospheres.

Processing and Dopant Effects on SiAlON

We have systematically investigated the effect of powder processing on the densification, microstructure and final properties of α-SiAlON ceramics. Due to the more restricted phase field of α-SiAlON, oxidation during powder processing has a major influence on the firing and final phase assemblage of the ceramic. This aspect has been documented and processing methods that minimize powder oxidation while allowing homogenization have been developed. We have also investigated the role of cation and anion dopants, at the level of

1000 ppm or less, to understand their effect on processing, microstructure development and final properties. We have found evidence that the currently popular notion of cation interfacial segregation is rather misleading, and is insufficient to form the basis of material design. A new model founded on glass structure and property has been proposed to explain the dopant effects on SiAlON ceramics.

Other Ceramics

Cellular Ceramic Composites

Ceramic layer composites have outstanding mechanical properties due to either an advantageous combination of the constituent properties or to the weak interface engineered into the layer structure. The major drawback, however, is on the processing side because of the need of laminating in the green state, the relative poor sintering performance (delamination and shrinkage cracks), and the thickness restriction due to handling requirements. To circumvent these problems, we have recently developed a new method for fabricating ceramic laminates based on deformation processing (repeated rolling and folding) in the green state at room temperature. A surprising finding of this work is that novel cellular microstructures containing discontinuous layer phases can also be obtained by the same method. The initial work was performed using aqueous slurries. We have now demonstrated a similar approach using ceramic suspensions in paraffin-oil/paraffin which are more suitable for ceramics that are water sensitive. Both ceramics with strong layer interface and weak layer interface have been obtained. High bending strength was achieved in the former case and graceful failure was achieved in the latter case. This class of materials is equivalent to the famed Damascus Sword but is made of ceramics initially processed at low temperatures.

Nucleation and Growth of β-Si_3N_4/β-SiAlON Crystals from Liquid

The kinetics of nucleation and growth of β-Si_3N_4/β-SiAlON crystals from liquid in the (Y,Mg)(Si,Al)(O,N) has been studied and surprising results have been obtained. We found, for the first time, definitive evidence of nucleation control by α-Si_3N_4 powders in the liquid, in contradiction to the conventional thinking on β-Si_3N_4 ceramics. This is the result of a very large supersaturation (at about 10 times the equilibrium concentration), which can be sustained in the glassy liquid but not in the ceramics. The coarsening kinetics was also found to be surprisingly robust, not showing the deceleration expected for Oswald ripening. This is because of the concomitant conversion of β-Si_3N_4 to β-SiAlON, which provides an additional source of driving force that overwhelms the capillary driving force. The kinetics have been analytically modeled and found in good with the observed particle size statistics.

Effect of Grain Boundary Sliding on Diffusional Creep

Diffusional creep occurs by redistribution of matter in response to normal stresses at grain boundaries, which are the source and sinks of atoms. The stress distribution is affected by grain boundary sliding, which itself also contributes to deformation. The role of grain boundary sliding in overall diffusional creep of a polycrystal has been evaluated using a theoretical approach that rests on the energy partition between shear and normal displacement modes. This approach readily allows the consideration of grain boundary viscosity, which is dependent on grain boundary geometry (e.g., liquid film thickness) and chemistry (e.g., F) in silicon nitride. The transition from normal displacement control to shear control has been demonstrated.

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Personnel Supported

I-Wei Chen	Principal Investigator
Roman Shuba	PhD student (graduated in 2005, now at GE Central R&D)
Byung-Nam Kim	Visiting scientist (on leave from National Institute for Materials Science, Japan, returned to Japan)
Misha Zenotchkine	Visiting scientist (returned to Russia)

Publications

(a) M. Zenotchkine, R. Shuba, J-S. Kim and I-Wei Chen, "R-Curve Behavior of In-situ Toughened α-SiAlON Ceramics," J. Am. Ceram. Soc., **84** [4] 884-86 (2001).

(b) M. Zenotchkine, R. Shuba, J-S. Kim and I-Wei Chen, "Synthesis of α-SiAlON Seed Crystals," J. Am. Ceram. Soc., **84** [7] 1651-53 (2001).

(c) I-W. Chen and E.J. Winn, "Delaminating Oxide Layered Composites with Wavy Interfaces," Z. Metallk., **92**, 757-61 (2001).

(d) I-Wei Chen and R. Shuba, "Structures and Properties of α-SiAlON Ceramics," in Encyclopedia of Materials: Science and Technology, Ed. K. H. J. Buschow, R,.W. Cahn, M. C. Flemings, B. Ilschner, E. J. Kramer and S. Mahajan, Elsevier Science , 2001, pp. 8471-76.

(e) A. Pechenik and I-W. Chen, "Advanced Silicon Nitride Ceramics", Advanced Materials and Processing, p. 37, March (2001).

(f) I-W. Chen, E.J. Winn and M. Menon, "Application of Deformation Instability to Microstructural Control in Multilayer Ceramic Composites," *Mater. Sci. Eng.*, **A317**, 226-35 (2001).

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(h) A. Dakskobler, T. Kosmac and I-W. Chen, "Paraffin-based Process for Processing Layered Composites with Cellular Microstructures," J. Am. Ceram. Soc., **85** [4], 1013-15 (2002).

(i) M. Zenotchkine, R. Shuba, and I-W. Chen, "Effect of Heating Schedule on the Microstructure and Fracture Toughness of α-SiAlON: Cause and Solution," *J. Am. Ceram. Soc.*, **85** [7] 1882-84 (2002).

(j) M. Zenotchkine, R. Shuba, J-S. Kim and I-W. Chen, "Effect of Seeding on the Microstructure and Mechanical Properties of α-SiAlON: I. Y-SiAlON," J. Am. Ceram. Soc., **85** [5] 1254-59 (2002).

(k) M. Zenotchkine, R. Shuba, J-S. Kim and I-W. Chen, "Effect of Seeding on the Microstructure and Mechanical Properties of α-SiAlON: II. Ca-SiAlON," J. Am. Ceram. Soc., **85** [5] 1260-67 (2002).

(l) M. Zenotchkine, R. Shuba, and I-W. Chen, "Effect of Seeding on the Microstructure and Mechanical Properties of α -SiAlON: III. Comparison of Modifying Cations," *J. Am. Ceram. Soc.* **86** [7] 1168-75 (2003).

(m)I-W. Chen, L. Wang and A. Davenport, "Accelerated Precipitate Coarsening due to a Concomitant Secondary Phase Transformation," *Acta Materialia*, **51** [6] 1691 - 1703 (2003).

(n) L. Wang, T-Y. Tien, and I-W. Chen, "Formation of Beta Silicon Nitride Crystals from (Si,Al,Mg,Y)-(O,N) Liquid--I. Phase, Composition and Shape Evolutions," *J. Am. Ceram. Soc.* **86** [9] 1578-85 (2003).

(o) L-L. Wang, T-Y. Tien, and I-W. Chen, "Formation of Beta Silicon Nitride Crystals from (Si,Al,Mg,Y)-(O,N) Liquid-- II. Population Dynamics and Coarsening Kinetics," *J. Am. Ceram. Soc.* 86 [9]1586-91 (2003).

(p) I-W. Chen, R. A. Shuba, M. Y. Zenotchkine, "Development of Tough α-SiAlON," *Key Eng. Mat.* 237, 65-78 (2003).

(q) M. Zenotchkine, R. Shuba, and I-W. Chen, "Liquid Phase Growth of Small Crystals for Seeding α-SiAlON Ceramics," *J. Am. Ceram. Soc.* 87 [6] 1040-46 (2004).

(r) J. Yu, H. Du, R. Shuba and I-W. Chen, "Dopant Dependent Oxidation Behavior of α-SiAlON," *J. Mater. Sci.* **39**, 4855-60 (2004 (2004).

(s) Five manuscripts derived from a recent thesis are in preparation.

TRANSITIONS/PATENTS

Samples of *in-situ* toughened α-SiAlON have been provided to several US manufacturing and engineering concerns to evaluate their performance. This evaluation process is on-going as the performance is application-specific, depending on the condition, environment and material system. Thus, composition, microstructure and property optimization is required for each application (e.g., cutting tool, bearing, surface wear).

Samples of *in-situ* toughened α-SiAlON have been provided to Dr. Paul Becher of Oak Ridge National Laboratory to evaluate the thermal expansion coefficients. A large effect of dopants and seeding has been found, which makes it possible to tailor the ceramics to have different thermal expansion behavior. A preliminary report to the Department of Energy has been submitted to document these results. (Not cited here.)

Collaborative research with Prof. R. Riedel of Damstadt Technical University of Germany has resulted in the discovery of a new structure of solid solution of Si-Al-O-N. A patent application has been filed with Prof. Chen as a co-inventor.

Collaborative research with Prof. H. Du of Stevens Institute of Technology has been ongoing to investigate the oxidation resistance of α-Sialon. Certain compositions were found to perform favorably compared to the state-of-the-art commercial β-Si_3N_4. A manuscript has been published to report the first results. Additional compositions have been selected for further mechanistic studies and for friction studies.

Outreach

The PI gave a Keynote lecture, "Development of Tough α-SIALON," in the International Symposium on SIALONS, Chiba, Japan, December 2001.

<u>Other selected invited talks by PI</u>

"Microstructure Development in Silicon Nitride-Issues and Plausible Resolutions," in the annual meeting of the American Ceramic Society, St. Louis, April-May 2002.

"Recent Advances in Tough α-SIALON," in the Annual Meeting of the American Ceramic Society, Centennial Celebration Symposium of First Flight, Nashville, May 2003.

"Processing and Properties of Advanced Ceramics and Nanoceramics," JSPS International Workshop on Advanced Ceramics, Atami, Japan, November 2003.

"Optimization of Thermomechanical Properties of α-SiAlON," in the International Symposium on New Frontiers of Advanced Si-Based Ceramics and Composites, Gyeongju, Korea, June 2004.

<u>Awards and Honors of PI</u>

Academician of World Academy of Ceramics (2004)

Sosman Award, American Ceramic Society (2006)